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Organic photovoltaic devices produced from conjugated polymer / methanofullerene bulk heterojunctions

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Abstract

Organic photovoltaic devices have been fabricated utilizing the photoinduced electron transfer with long-living charge separation in conjugated polymer/methanofullerene thin films. The performance of such "bulk heterojunction" photovoltaic devices is critically dependent on the charge transport properties of the interpenetrating network. Devices with power efficiencies higher than 2.5 % under AM1.5 have been realized. The physical properties of these bipolar devices are discussed with respect to the transport properties of the network. Further possible enhancement is discussed by analyzing the single parameters contributing to the AM 1.5 efficiency in plastic solar cells, namely, the open circuit voltage (V_{oc}), the short circuit current (I_{sc}), the fill factor (FF) as well as the absorption matching to the solar spectrum.

Keywords: Plastic Solar Cells, Poly (phenylene vinylene) and Derivatives, Fullerenes and Derivatives, Bulk heterojunction, Photoconductivity, Metal / Semiconductor Interfaces

1. Introduction

The operation of an organic photovoltaic device may be visualized as taking place in three consecutive fundamental steps: (1) absorption of light, (2) creation of separate charges at the donor – acceptor interfaces, and (3) selective transport of the charges through the bulk of the device to the appropriate collecting electrodes. A prerequisite for high efficiency for the conversion of photons into electrical current is that the holes and electrons do not recombine before being swept out of the device to the external circuit. Therefore, a metastable photoinduced charge-separated state and high charge carrier mobilities are important factors. A conjugated polymer – methanofullerene blend can provide both of these characteristics [1]. Time-resolved measurements [2] have shown that the initial photoinduced electron transfer from a conjugated polymer to a soluble methanofullerene occurs on the timescale of 50 fs, whereas the timescale for back transfer to the neutral state is very long and extends into the milliseconds range. Once this metastable charge-separated state is formed, the free charges are transported through the device through diffusion and drift processes. The latter is induced by using top and bottom layer electrodes that have different work-functions, thus providing a built-in electric field over the active layer. In the active layer of the device, holes are transported through the conjugated polymer matrix, and electrons are transported by hopping between fullerene molecules. Importantly, these two different charge transport processes do not interfere with each other which has been proved by recent mobility measurements.

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The overall efficiency η_{eff} of a solar cells is calculated by the following formula:

$$\eta_{eff} = V_{oc} * I_{sc} * FF / I_{light}$$

where Voc is the open circuit voltage, Isc the short circuit current in A/m^2, FF the fill factor and I_{light} the incident solar radiation in W/m^2. Also the new generation of plastic solar cells with efficiencies over 2.5% as published recently [3] have intrinsic loss mechanisms. In this contribution further possible strategies to improve the overall efficiency of plastic solar cells based upon bulk heterojunctions are discussed.

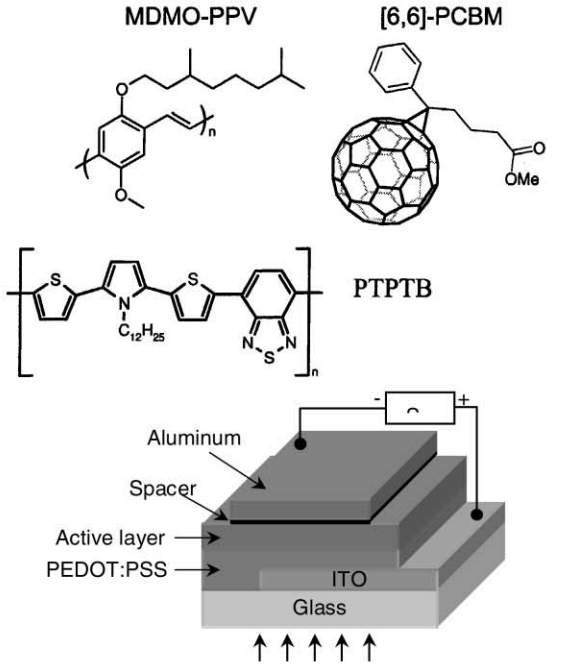

Figure 1: Chemical structure of Plastic Solar Cell materials as well as the device structure.

2. Experimental

The chemical structure of the compounds and the device structure is shown in Figure 1. For the solar cells reported here we used poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene - vinylene) (MDMO-PPV) or poly-(thiophene-pyrrole-thiophene-benzothiadiazole) (PTPTB) as electron donor, while the electron acceptor was [6,6]-Phenyl C_{61} - butyric acid methyl ester [4] (PCBM) both of which show satisfactory solubility in a large number of organic solvents.

The enhanced solubility of PCBM compared to C_{60} allows a high fullerene to conjugated polymer ratio. ITO / glass substrates (MDT) were cleaned in ultrasonic baths of acetone, methanol and isopropanol, followed by oxygen plasma treatment. Poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid (PEDOT:PSS, Bayer AG) was spin-coated to a thickness of 100 nm on top of the ITO from a water solution. The active layer consisting of MDMO-PPV : PCBM (1:4 by wt.) was spin-coated on top of the PEDOT to a thickness of 100 nm from solution. The aluminum cathode was thermally deposited through a shadow mask to define a device area of 7.5 mm^2 after evaporation of a thin LiF layer. Device fabrication was performed in an argon dry-box.

Photovoltaic devices were illuminated with a solar simulator (Solar Constant 575 with AM1.5 filter, K. H. Steuernagel Lichttechnik GmbH). The intensity was measured using a calibrated single-crystal Si solar cell (certified by ISE Institute für Solare Energieforschung, Freiburg). I-V characteristics were taken with a source-meter (Keithley 2400) at 50° C. For measurements of external quantum efficiency versus wavelength, devices were illuminated with a Xe lamp (Müller GmbH LXH 100) attached to a monochromator (Acton Research Corporation SpectraPro-150). Photocurrent was measured using an optical chopper (Scitec Instruments LTD) and lock-in detection (EG&G Instruments 7260) at 25° C.

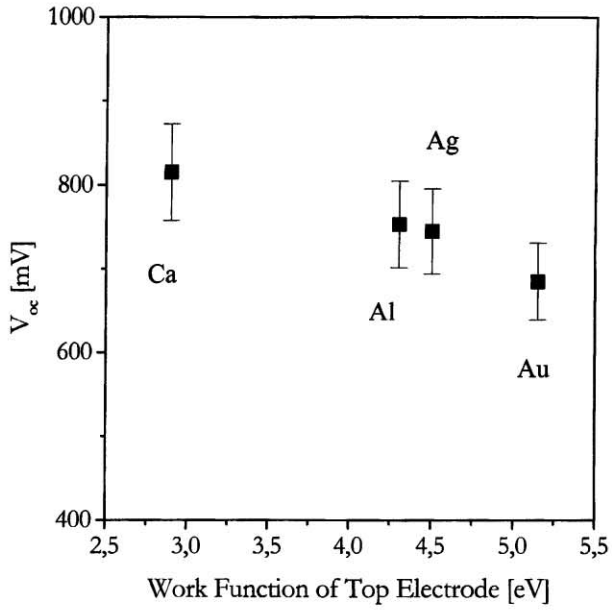

Figure 2: Typical relation between V_{oc} versus top metal work function for the photodiodes. The relative errors are within 5 %.

3. Results & Discussion

The open circuit voltage

A highly interesting phenomenon in the Plastic Solar Cells (PSC) is the observation of unusual high open circuit voltages. Before discussing the observations in PSC, we briefly review the findings for pristine conjugated polymer PV elements.

For single layer polymer PV elements, produced by spin casting from alkoxy PPV solutions, a consistent picture is found for the experimental observation and an explanation of the open circuit voltage is given. For devices with high purity ($N_d << 10^{17}cm^{-3}$), Parker argues [5], that single layer polymer devices work as Metal – Insulator - Metal (MIM) diodes. Typical, such devices exhibit a V_{oc} determined by the difference of the work functions of the two metal electrodes. On the other hand, for diodes prepared from PPV precursor, deviations from the MIM picture have been observed. Several groups [6] report on the observation of V_{oc} in the range of 1.2 – 1.5 V for ITO / precursor-PPV / Al devices and the formation of a Schottky junction at the precursor-PPV / Al interface was proved. We conclude, that the MIM picture is reasonable for pristine polymer PV devices as long as the impurity density does not favor the formation of Schottky barriers.

Experimentally observed V_{oc} of PSC could not be explained by the MIM picture. For typical devices, based on ITO / conj. Polymer – fullerene / Al, V_{oc} in the range of 700 mV and higher were reported for several polymer / fullerene mixtures, in contrast to the 400 mV expected from the MIM picture. Figure 2 shows the dependence of the open circuit voltage on the metal work function.
Typically, a V_{oc} of ~ 800 mV is observed for PSC, quite independent of the metal top electrode used. Ca, Al and Ag yield similar values, only Au is slightly lower. It is interesting to note, that even for Au the flow direction of the current was not reversed (electrons to Au, holes to ITO). Such behavior is interpreted by a pinning mechanism of the top metal electrode.

The short circuit current

A key parameter for the efficient charge collection of plastic solar cells is the hole and the electron mobility of the interpenetrating networks.

Figure 3 shows a calculation of the possible short circuit current in plastic solar cells, assuming that bimolecular recombination plays a negligible role. This assumption allowed to solve the diffusion equation separately for the hole and for the electron current. The absorption coefficient was estimated with 5* 10^4 cm^{-1}, temperature was set to 298 K, and the built in potential was estimated with 0.8 V. The quantum efficiency for charge generation was taken as unity. The boundary conditions were set to ensure no hole current to the anode (Al) and no electron current to the cathode (ITO/PEDOT) and to guarantee a negligible carrier gradient at the charge collecting electrode (field driven device).

The calculations show a clearly observable peak for the maximum short circuit current versus the device thickness. Depending on the given mobility, the peak shifts to larger values in the device thickness, thereby allowing to absorb more photons and yielding a larger total short circuit current. The calculated value of Isc with ~ 10 mA/cm^2 for a given mobility of 10^{-4} cm^2/Vs is in rather good correlation with the values measured for the new generation of the MDMO-PPV / PCBM solar cells. Devices with an open circuit potential of ≈0.8V and a short circuit current of ≈5 mA/cm^2 under an illumination of 80 mW/cm^2 using a solar simulator (Fa. Steuernagel) can be routinely fabricated now.

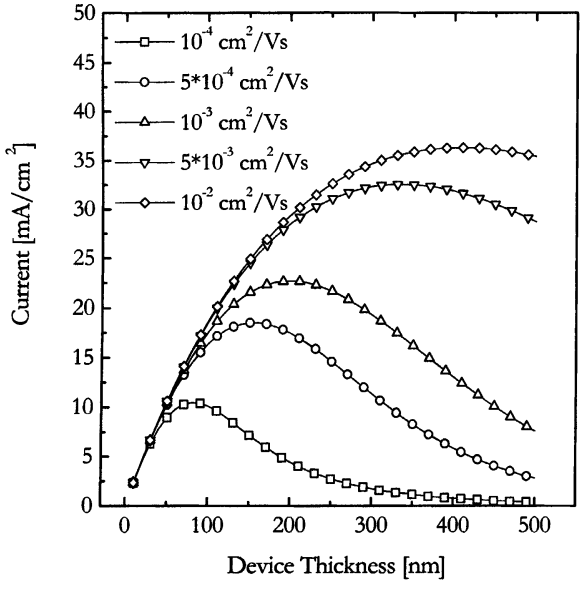

Figure 3: Calculated I_{sc} versus device thickness for different hole mobilities of the conjugated polymer. The mobilities are denoted inside the figure.

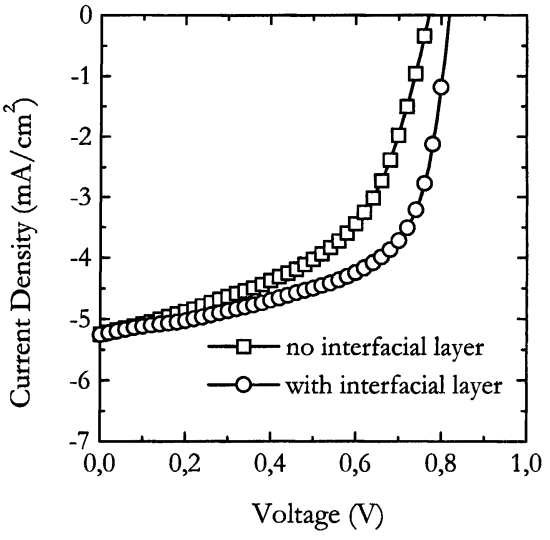

Figure 4: I/V plot of ITO / PEDOT / MDMO-PPV - PCBM /Al solar cells with and without an interfacial layer (LiF) between the Al electrode and the photoactive material.

The fill factor

The fill factor of solar cells as determined by

$$FF = I_{mpp} * V_{mpp} / I_{sc} * V_{oc}$$

with I_{mpp} and V_{mpp} as the current and the voltage in the maximum power point of the I/V curve in the 4th quadrant, reflects the diode properties of the solar cells.

In general, a large serial resistance as well as a too small parallel resistance (shunt) tend to reduce the FF. From LEDs, protective interface layers like LiF or SiO_x are well known to reduce the interface barrier for electron injection at the cathode, if they are evaporated between the photoactive material and an Al electrode[7]. Figure 4 shows the enhancement of the diode properties of a MDMO-PPV / PCBM solar cell under illumination with 80 mW/cm^2 from a solar simulator. While the short circuit current is left almost unchanged and only a small increase in the open circuit voltage is observed (from 780 to 820 mV) due to the interfacial layer, the FF is increased from 0.5 to 0.62. Also remarkably, the serial resistance of the devices with an interfacial layer (LiF) dropped down from ~ 200 - 400 Ohm to ~ 40 – 50 Ohm.

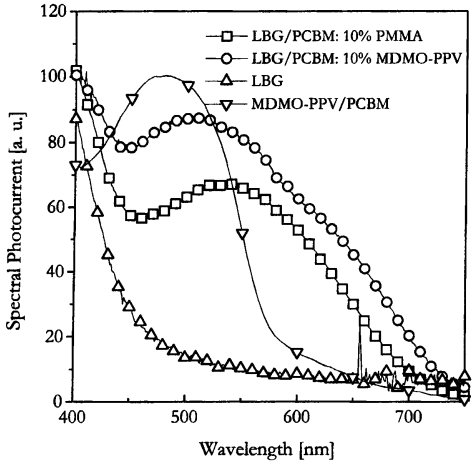

Figure 5: spectrally resolved photocurrent of a photodiode, where the active layer, either a low bandgap polymer LBG, or LBG/PCBM/PMMA or LBG/PCBM/MDMO-PPV or MDMO-PPV/PCBM is sandwiched between ITO/ PEDOT and Al

Spectral Sensitization

One of the limiting parameters in plastic solar cells is their mismatch to the solar spectrum. Typically, conjugated polymers like MDMO-PPV, used for photovoltaics have their peak absorption around 500 nm which is clearly offset to the maximum in the photon flux of the sun, which peaks around 700 nm.

The use of low bandgap polymers (E_g <1.8 eV) to expand the spectral region of bulk heterojunction solar cells is suggested in this work. These polymers can enhance the spectral range by a direct mechanism like a photoinduced charge transfer to the fullerene. The charge transport to the electrodes will occur via the polymer as well as the fullerene.

Fig 5 shows the spectrally resolved photocurrent for a photodiode from low band gap polymer (see fig. 1) with and without PCBM. Spectra are normalized to their peak values. While the photocurrent generation for the pristine PTPTB device has the maximum at low wavelengths with a small tail extending to the IR, the PTPTB/PCBM/PMMA device shows efficient charge carrier generation in the region from 500 – 700 nm, resembling the absorption profile of the polymer. PMMA was used to improve the film quality. For a device with PMMA instead of MDMO-PPV as host polymer, the spectral photocurrent is observed to show contributions from both polymers, thereby indicating that both polymers undergo photoinduced charge transfer to the methanofullerene. The photocurrent of a MDMO-PPV / PCBM device is plotted as reference.

4. Conclusion

Bulk heterojunction plastic solar cells with efficiencies > 2.5 % and short circuit current of ~ 5 mA/cm^2 under AM 1.5 illumination from a solar simulator can be produced routinely by spin casting from solution. While 2.5 % is already a promising value, improvement strategies were suggested for further optimisation of polymeric photovoltaic systems based on the bulk heterojunction principle.

5. Acknowledgement

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